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(54) **Acid tin-silver alloy electroplating bath and method for electroplating tin-silver alloy**

Saures Zinn-Silber-Legierung-Elektroplattierungsbad und Verfahren zur Elektroplattierung einer
Zinn-Silber-Legierung

Bain acide pour le dépôt électrolytique d'un alliage étain-argent et procédé de dépôt électrolytique
d'un alliage étain-argent

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(56) References cited:
EP-A- 0 666 342

EP 0 854 206 B1

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Description

[0001] The present invention relates to an acid, tin-silver alloy plating bath substantially non-cyanide and a method for electroplating Tin-Silver alloy onto a substrate.

5 [0002] As tin-silver alloy plating baths used for forming a tin-silver alloy plating film on a metal substrate or the like, an alkaline cyanide bath has been known.

[0003] However, since the bath contains the poisonous cyanide, the bath has problems that the bath per se has an extremely high toxicity which necessitates a special care in the handling and a special treatment of the waste water and that the working environment is polluted.

10 [0004] On the other hand, known non-cyanide acid baths, for example, include an alkanesulfonic acid or alkanolsulfonic acid bath, and mercaptoalkanecarboxylic acid and/or mercaptoalkanesulfonic acid as disclosed in Japanese Patent Unexamined Published Application (hereinafter referred to as "J. P. KOKAI") Nos. Hei 7-252684 (corresponding to EP-A-0 666 342) and Hei 8-13185.

15 [0005] However, in such an acid bath, it was impossible to form a stable solution by dissolving silver which is an indispensable component for forming the tin-silver alloy together with tin. Namely, silver was insolubilized to form a black or brown precipitate immediately after or within 24 hours after the preparation of the plating bath. It was thus difficult to maintain the concentration of the components in the bath.

20 [0006] After intensive investigations, the present applicant had developed an acid bath which was an alkanesulfonic acid and/or sulfamic acid bath containing a thioamide compound and a thiol compound. Although silver is not precipitated or insolubilized immediately after the preparation of the plating bath or in 24 hours thereafter, the plating bath has a problem that the thioamide compounds and the thiol compounds such as mercaptosuccinic acid and mercaptolactic acid exert a harmful influence on the plating properties when the plating bath is left to stand or kept being used for a long period of time.

25 [0007] When the acid bath is left to stand at a high temperature, silver is insolubilized to form the black or brown precipitate within 24 hours like in the acid baths disclosed in the above-described J. P. KOKAI Nos. Hei 7-252684 and 8-13185 and thus, it is difficult to keep the concentration of each component in the bath.

[0008] A primary object of the present invention is to provide a tin-silver alloy plating bath in which tin and silver can be kept dissolved therein in a stable state for a long period of time even at a high temperature and which is capable of keeping a predetermined plating capacity for a long period of time even though the bath is free from a cyan compound.

30 [0009] Another object of the present invention is to provide an effective method for electroplating Tin-Silver alloy onto a substrate.

[0010] These and other objects of the present invention will be apparent from the following description and Examples.

[0011] The present invention has been completed on the basis of a finding that a specific aromatic sulfur compound is effective in dissolving both tin and silver in a substantially non-cyanide acid bath to form a stable solution.

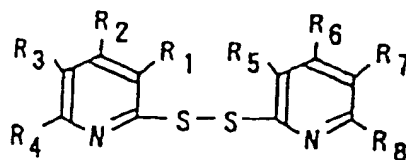
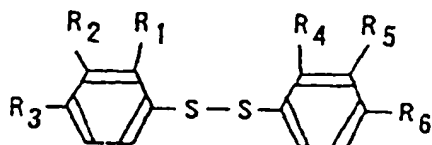
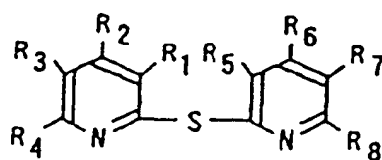
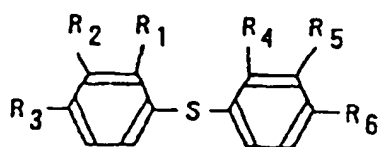
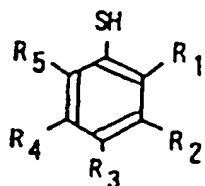
35 [0012] Namely, the present invention provides an acid tin-silver alloy plating bath which comprises a tin ion, a silver ion, one compound selected from aromatic thiol compounds and aromatic sulfide compounds, and a balance of water, the pH of the bath being not high than 2 and the bath being substantially cyanide free.

40 [0013] The present invention further provides a method for electroplating a Tin-Silver alloy on a substrate, which method comprises the steps of immersing the substrate as the cathode and a plate of a tin-silver alloy or tin plate as the anode in an acid tin-silver alloy plating bath which comprises a tin ion, a silver ion, one compound selected from aromatic thiol compounds and aromatic sulfide compounds, substantially no cyan compounds and a balance of water, the pH of the bath being not higher than 2, and charging electric current of about 0.5 to 50 A thereto for about 0.5 to 10 minutes to form onto the substrate a tin-silver alloy film comprising from 20 to 99 % by weight of tin and from 80 to 1 % by weight of silver and having a thickness of from 1 to 30 μm .

45 [0014] The tin compounds usable in the present invention are not particularly limited so far as they are capable of releasing tin ion in the acid bath. They include, for example, stannous oxide, stannous sulfate, tin chlorides, tin sulfides, tin iodides, tin citrates, tin oxalates and stannous acetate. They are used either singly or in the form of a mixture of two or more of them. Although the tin ion concentration in the plating bath is not particularly limited, it is preferably 2 to 80 g/l, more preferably 10 to 40 g/l (in terms of tin).

50 [0015] The silver compounds usable in the present invention are not particularly limited so far as they are capable of releasing silver ion in the acid bath. They include, for example, silver oxides, silver sulfates, silver chlorides and silver nitrates. They are used either singly or in the form of a mixture of two or more of them. Although the silver ion concentration in the plating bath is not particularly limited, it is preferably 0.01 to 80 g/l, more preferably 0.1 to 50 g/l (in terms of silver).

55 [0016] The aromatic thiol compounds and aromatic sulfide compounds used in the present invention are preferably those having 6 to 14 carbon atoms. In particular, at least one of the compounds having the following structures is preferably used:



wherein R_1 to R_8 each represent a hydrogen atom, lower alkyl group (preferably having 1 to 3 carbon atoms), hydroxyl group, nitro group, amino group or thiol group.

[0017] More specifically, the aromatic thiol compounds usable in the present invention include, for example, thiophenol, mercaptophenol, thiocresol, nitrothiophenol, thiosalicylic acid, aminothiophenol, benzenedithiophenol and mercaptopyridine. They are used either singly or in the form of a mixture of two or more of them.

[0018] The aromatic sulfides are preferably aromatic mono- or disulfide compounds such as 4,4-thiodiphenol, 4,4-aminodiphenyl sulfide, thiobisthiophenol, 2,2-diaminodiphenyl disulfide, 2,2-dithiodibenzoic acid, ditolyl disulfide and 2,2-dipyridyl disulfide. They are used either singly or in the form of a mixture of two or more of them.

[0019] The aromatic thiol compounds and aromatic sulfides are more preferably those having NH_2 group in the substituent in the structure thereof or those having a pyridine ring in the structure thereof.

[0020] Either or both of the aromatic thiol compound or/and aromatic sulfide compound is usable in the present invention. Further a mixture of two or more of the aromatic thiol compounds or aromatic sulfide compounds is also usable. These compounds are capable of imparting a gloss to the resultant deposit, too.

[0021] The amount of each of the aromatic thiol compound and aromatic sulfide compound used in the present invention is not particularly limited so far as both tin and silver dissolved in the bath can be kept stable. It is preferably 0.1 to 200 g/l, more preferably 0.2 to 50 g/l.

[0022] An acid substance can be incorporated into the tin-silver alloy plating bath in order to control the pH of the bath on acidic side. The acid substances are preferably alkanesulfonic acids having 1 to 3 carbon atoms such as methanesulfonic acid, ethanesulfonic acid and hydroxypropanesulfonic acid; benzenesulfonic acids and phenolsulfonic acids having 6 or 7 carbon atoms such as sulfosalicylic acid and cresolsulfonic acid; alkanolsulfonic acids such as isopropanolsulfonic acid; and sulfamic acid. These acids are usable either singly or in the form of a mixture of two or more of them. Although the acid concentration in the plating bath is not particularly limited so far as tin and silver are soluble therein, it is preferably 10 to 500 g/l, more preferably 50 to 400 g/l. In particular, the acid concentration in the

plating bath is controlled so that the pH of the bath can be kept not higher than 2, preferably not higher than 1.

[0023] The plating bath of the present invention can comprise the above-described indispensable components and the balance of water and, if necessary, additives such as a brightening agent and lubricating agent. The brightening agent may be any of those used for brightening tin and silver such as nonionic surfactants, anionic surfactants, synthetic polymers (e. g. PVP, PEG and PVA), amines (e. g. hexamethylenetetramine and triethanolamine), ketones (e. g. benzalacetone and acetophenone), aliphatic aldehydes (e. g. formalin and valeric aldehyde), aromatic aldehydes (e. g. salicylaldehyde and vanillin) and metal compounds containing Sb, Se, Cu, In, Zn, Ca, Ba or the like. These compounds are usable either singly or in the form of a mixture of two or more of them. The amount of the brightening agent is preferably 0.5 to 50 g/l, more preferably 0.2 to 30 g/l.

[0024] Antioxidants for tin are also usable. They include hydroxyphenyl compounds such as phenol, catechol, pyrogallol and hydroquinone; L-ascorbic acid; and sorbitol.

[0025] The acid tin-silver alloy plating bath of the present invention are usable for plating various substrates such as iron or copper substrates by an ordinary method to form the tin-silver alloy deposit. In particular, the substrate as the cathode and a plate of a tin-silver alloy or tin plate as the anode are immersed in the tin-silver alloy plating bath and then electric current of about 0.5 to 50 A is sent for about 0.5 to 10 minutes to form a tin-silver alloy film comprising 20 to 99 % by weight of tin and 80 to 1 % by weight of silver and having a thickness of 1 to 30 μ m.

[0026] The tin-silver alloy plating bath of the present invention has an advantage that it has only a low toxicity and a high safety because it is of a non-cyan type unlike an ordinary alkaline cyan bath. In addition, although silver easily forms insoluble salts with various substances, the tin-silver alloy plating bath of the present invention can be kept stable for a long period of time without changing the plating function thereof. Another advantage of this plating bath is that since it does not necessitate any special treatment of the waste water, the waste water treatment cost is low.

[0027] When the tin-silver alloy plating bath of the present invention is used as an electroplating bath, a thin film having a thickness of 1 to 30 μ m is obtained unlike a film formed by a hot dipping technique. Thus, according to the present invention, even precision parts can be plated and a high workability can be attained advantageously.

[0028] The following Examples will further illustrate the present invention.

Example 1

[0029] An acid tin-silver alloy plating bath comprising the following components and the balance of water was prepared (pH: not higher than 1):

| | |
|----------------------|---------|
| SnO | 30 g/l |
| methanesulfonic acid | 350 g/l |
| Ag ₂ O | 2 g/l |
| 2-aminobenzenethiol | 20 g/l |

Example 2

[0030] An acid tin-silver alloy plating bath comprising the following components and the balance of water was prepared (pH: not higher than 1):

| | |
|-------------------------|---------|
| SnO | 30 g/l |
| methanesulfonic acid | 350 g/l |
| Ag ₂ O | 1 g/l |
| 2,2-dipyridyl disulfide | 5 g/l |

Example 3

[0031] An acid tin-silver alloy plating bath comprising the following components and the balance of water was prepared (pH: not higher than 1):

| | |
|-------------------------|----------|
| SnO | 30 g/l |
| methanesulfonic acid | 1150 g/l |
| Ag ₂ O | 1 g/l |
| 2,2-dipyridyl disulfide | 5 g/l |

(continued)

| | |
|--|---------|
| nonionic surfactant (SEDORAN FF-180; a product of Sanyo Chemical Industries, Ltd.) | 4 g/l |
| benzalacetone | 1.5 g/l |

Example 4

[0032] An acid tin-silver alloy plating bath comprising the following components and the balance of water was prepared (pH: not higher than 1):

| | |
|---|---------|
| SnO | 10 g/l |
| hydroxypropanesulfonic acid | 150 g/l |
| Ag ₂ O | 10 g/l |
| 2-aminobenzenethiol | 5 g/l |
| nonionic surfactant (EPAN 450; a product of Dai-ichi Kogyo Seiyaku Co., Ltd.) | 5 g/l |
| 35 % formalin | 10 g/l |
| triethanolamine | 5 g/l |
| potassium antimonyl tartrate | 0.1 g/l |

Example 5

[0033] An acid tin-silver alloy plating bath comprising the following components and the balance of water was prepared (pH: not higher than 1):

| | |
|---|---------|
| SnO | 30 g/l |
| isopropanolsulfonic acid | 250 g/l |
| Ag ₂ O | 3 g/l |
| 2-aminobenzenethiol | 5 g/l |
| nonionic surfactant (EPAN 450; a product of Dai-ichi Kogyo Seiyaku Co., Ltd.) | 6 g/l |
| piperonal | 0.1 g/l |

Comparative Example 1

[0034] An acid tin-silver alloy plating bath comprising the following components and the balance of water was prepared (pH: not higher than 1):

| | |
|----------------------|---------|
| SnO | 30 g/l |
| methanesulfonic acid | 150 g/l |
| Ag ₂ O | 2 g/l |

Comparative Example 2

[0035] An acid tin-silver alloy plating bath comprising the following components and the balance of water was prepared (pH: not higher than 1):

| | |
|--------------------------|---------|
| SnO | 30 g/l |
| isopropanolsulfonic acid | 150 g/l |
| Ag ₂ O | 5 g/l |

Comparative Example 3

[0036] An acid tin-silver alloy plating bath comprising the following components and the balance of water was prepared (pH: 3.2):

| | |
|---------------------------------------|--------|
| SnCl ₄ · 5H ₂ O | 30 g/l |
| AgNO ₃ | 63 g/l |
| thiomalic acid | 90 g/l |
| potassium citrate | 26 g/l |

[0037] KOH and NaOH were used in a weight ratio of 1:1 for controlling pH.

Comparative Example 4

[0038] An acid tin-silver alloy plating bath comprising the following components and the balance of water was prepared (pH: not higher than 1):

| | |
|----------------------|---------|
| SnO | 30 g/l |
| methanesulfonic acid | 150 g/l |
| Ag ₂ O | 2 g/l |
| thiourea | 3 g/l |

Comparative Example 5

[0039] An acid tin-silver alloy plating bath comprising the following components and the balance of water was prepared (pH: not higher than 1):

| | |
|---|---------|
| SnO | 30 g/l |
| methanesulfonic acid | 150 g/l |
| Ag ₂ O | 1 g/l |
| thiourea | 3 g/l |
| nonionic surfactant (SUNMORL BN-13D; a product of Nikka Kagaku) | 4 g/l |
| hexamethylenetetramine | 4 g/l |
| benzalacetone | 1.5 g/l |
| potassium antimonyl tartrate | 0.1 g/l |

[0040] The plating baths prepared in Examples 1 to 5 and Comparative Examples 1 to 5 were left to stand at room temperature. The formation of the precipitate in the plating bath was macroscopically observed and the silver concentration was analyzed by the atomic absorptiometry 4 hours, 10 days, 30 days and 120 days after.

[0041] The results are summarized in Table 1.

Table 1

| | Precipitation | | | | Silver conc. in bath (g/l) | | | |
|-------------|---------------|----|----|----|----------------------------|------|------|------|
| | a. | b. | c. | d. | a. | b. | c. | d. |
| Ex. 1 | ○ | ○ | ○ | ○ | 1.86 | 1.86 | 1.85 | 1.86 |
| Ex. 2 | ○ | ○ | ○ | ○ | 0.93 | 0.91 | 0.93 | 0.92 |
| Ex. 3 | ○ | ○ | ○ | ○ | 0.93 | 0.93 | 0.91 | 0.92 |
| Ex. 4 | ○ | ○ | ○ | ○ | 27.9 | 27.7 | 27.8 | 27.8 |
| Ex. 5 | ○ | ○ | ○ | ○ | 2.78 | 2.78 | 2.79 | 2.78 |
| Comp. Ex. 1 | × | × | × | × | 0.00 | 0.00 | 0.00 | 0.00 |
| Comp. Ex. 2 | × | × | × | × | 0.00 | 0.00 | 0.00 | 0.00 |
| Comp. Ex. 3 | ○ | × | × | × | 40.4 | 8.64 | 0.00 | 0.00 |
| Comp. Ex. 4 | ○ | ○ | ○ | ○ | 1.86 | 1.85 | 1.86 | 1.86 |
| Comp. Ex. 5 | ○ | ○ | ○ | ○ | 0.93 | 0.92 | 0.92 | 0.93 |

Table 1 (continued)

| | Precipitation | | | | Silver conc. in bath (g/l) | | | |
|--|---------------|----|----|----|----------------------------|----|----|----|
| | a. | b. | c. | d. | a. | b. | c. | d. |
| ○ : no precipitation × : precipitation a. 4 hours after the preparation of the plating bath: b. 10 days after the preparation of the plating bath: c. 30 days after the preparation of the plating bath: d. 120 days after the preparation of the plating bath: | | | | | | | | |

[0042] The plating baths prepared in Examples 1 to 5 and Comparative Examples 4 and 5 were left to stand at 60 °C. The formation of the precipitate in the plating bath was macroscopically observed and the silver concentration was analyzed by the atomic absorptiometry 4 hours, 10 days, 30 days and 120 days after.

[0043] The results are summarized in Table 2.

Table 2

| | Precipitation | | | | Silver conc. in bath (g/l) | | | |
|--|---------------|----|----|----|----------------------------|------|------|------|
| | a. | b. | c. | d. | a. | b. | c. | d. |
| Ex. 1 | ○ | ○ | ○ | ○ | 1.86 | 1.86 | 1.85 | 1.86 |
| Ex. 2 | ○ | ○ | ○ | ○ | 0.93 | 0.91 | 0.93 | 0.92 |
| Ex. 3 | ○ | ○ | ○ | ○ | 0.93 | 0.93 | 0.91 | 0.92 |
| Ex. 4 | ○ | ○ | ○ | ○ | 27.9 | 27.7 | 27.8 | 27.8 |
| Ex. 5 | ○ | ○ | ○ | ○ | 2.78 | 2.78 | 2.79 | 2.78 |
| Comp. Ex. 4 | × | × | × | × | 0.74 | 0.00 | 0.00 | 0.00 |
| Comp. Ex. 5 | × | × | × | × | 0.36 | 0.00 | 0.00 | 0.00 |
| ○ : no precipitation × : precipitation a. 4 hours after the preparation of the plating bath: b. 10 days after the preparation of the plating bath: c. 30 days after the preparation of the plating bath: d. 120 days after the preparation of the plating bath: | | | | | | | | |

[0044] The plating baths prepared in Examples 1 to 5 and Comparative Examples 4 and 5 were left to stand at room temperature. The Hull cell tests were conducted under the conditions shown below 4 hours, 10 days, 30 days and 120 days after.

Test conditions:

[0045]

| | |
|------------------|----------------------|
| bath temperature | 25 °C |
| anodic plate | tin plate |
| cathodic plate | polished steel plate |
| electric current | 3 A |
| plating time | 10 minutes. |

[0046] In the plating bath prepared in Comparative Example 4, crude precipitates were formed in a high-current density part and the relative amount of alloyed silver was increased in the tin-silver alloy with time, while no change in the appearance of the deposit or in the proportion of the tin to silver in the alloy with time was observed when the plating bath prepared in any of Examples 1 to 5 was used. When the plating bath prepared in Comparative Example 5 was used, the gloss and smoothness of the deposit were deteriorated and the relative amount of alloyed silver was decreased in the tin-silver alloy with time.

[0047] The relative amount of alloyed silver in the deposit was determined by the atomic absorptiometry in parts 1,

5 and 9 cm distant from the high-current density side of the Hull cell test panel. The results of the analysis are shown in Table 3.

Table 3

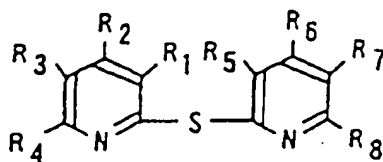
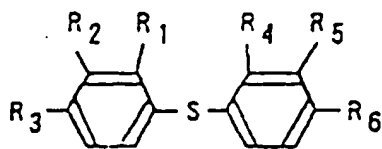
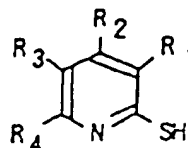
| Alloyed silver in deposit (wt. %) | | | | | | | |
|-----------------------------------|---------------------|------|------|---------------|------|-------|------|
| 4 hours after | | | | 10 days after | | | |
| <u>Distance from high current</u> | | | | | | | |
| | <u>density side</u> | 1cm | 5cm | 9cm | 1cm | 5cm | 9cm |
| Ex. 1 | | 8.6 | 6.4 | 2.5 | 8.5 | 6. 6 | 2.4 |
| Ex. 2 | | 4.2 | 3.4 | 1.8 | 4.3 | 3. 3 | 1.6 |
| Ex. 3 | | 3.5 | 3.3 | 2.9 | 3.6 | 3. 4 | 3.0 |
| Ex. 4 | | 36.7 | 24.5 | 18.8 | 37.8 | 25. 4 | 18.5 |
| Ex. 5 | | 12.6 | 9.8 | 7.2 | 12.8 | 9. 6 | 7.1 |
| Comp. Ex. 4 | | 7.8 | 5.5 | 2.8 | 8.5 | 6. 4 | 3.1 |
| Comp. Ex. 5 | | 5.6 | 3.4 | 1.9 | 4.4 | 2. 1 | 1.1 |

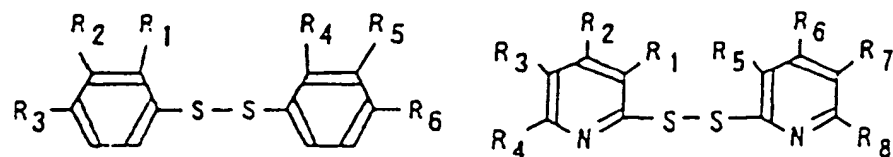
Table 3 (continued)

| Alloyed silver in deposit (wt. %) | | | | | | |
|-----------------------------------|------|------|------|----------------|------|------|
| 30 days after | | | | 120 days after | | |
| <u>Distance from high current</u> | | | | | | |
| density side | 1cm | 5cm | 9cm | 1cm | 5cm | 9cm |
| Ex. 1 | 8.7 | 6.3 | 2.5 | 8.6 | 6.4 | 2.6 |
| Ex. 2 | 4.0 | 3.3 | 1.6 | 4.2 | 3.4 | 1.7 |
| Ex. 3 | 3.5 | 3.4 | 2.9 | 3.5 | 3.4 | 2.9 |
| Ex. 4 | 36.5 | 24.9 | 18.5 | 36.8 | 24.7 | 18.7 |
| Ex. 5 | 12.7 | 9.7 | 7.3 | 12.6 | 9.8 | 7.3 |
| Comp. Ex. 4 | 9.8 | 6.9 | 3.7 | 9.7 | 7.0 | 3.8 |
| Comp. Ex. 5 | 3.6 | 1.6 | 0.9 | 3.4 | 1.4 | 0.8 |

Claims

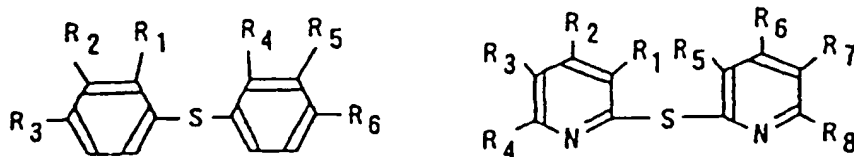
1. An acid tin-silver alloy plating bath which comprises a tin ion, a silver ion, one compound selected from aromatic thiol compounds and aromatic sulfide compounds, and a balance of water, the pH of the bath being not high than 2 and the bath being substantially cyanide free.
2. An acid plating bath as claimed in claim 1, wherein the aromatic sulfide compounds are aromatic mono- or disulfide compounds.
3. An acid plating bath as claimed in claim 1 or claim 2, wherein the aromatic thiol compounds and aromatic sulfide compounds have from 6 to 14 carbon atoms.
4. An acid plating bath as claimed in any one of claims 1 to 3, wherein the amount of the aromatic thiol compounds and aromatic sulfide compounds is from 0.1 to 200 g/l.
5. An acid plating bath as claimed in any one of claims 1 to 4, wherein the amount of the tin ion is from 2 to 80 g/l calculated as Sn.
6. An acid plating bath as claimed in any one of claims 1 to 5, wherein the amount of the silver ion is from 0.01 to 80 g/l calculated as Ag.
7. An acid tin-silver alloy plating bath as claimed in claim 1 which comprises from 2 to 80 g/l of a tin ion calculated as Sn, from 0.01 to 80 g/l of a silver ion calculated as Ag, from 0.1 to 200 g/l of one compound having from 6 to 14 carbon atoms selected from aromatic thiol compounds and aromatic sulfide compounds, substantially no cyan compounds and a balance of water, the pH of the bath being not higher than 2.
8. An acid plating bath as claimed in any one of claims 1 to 7, wherein the aromatic thiol compounds and aromatic sulfide compounds are selected from compounds having the following structure:

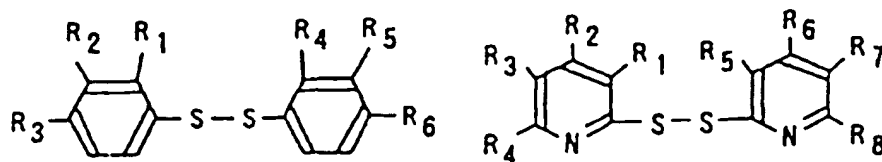




wherein R_1 to R_8 each represent a hydrogen atom, lower alkyl group, hydroxyl group, nitro group, amino group or thiol group.

9. An acid plating bath as claimed in any one of claims 1 to 8, which further contains an acid selected from the group consisting of alkanesulfonic acids, alkanolsulfonic acids and sulfamic acids.
10. An acid plating bath as claimed in claim 9, wherein the acid is present in an amount of from 10 to 500 g/l.
11. A method for electroplating a tin-silver alloy on a substrate, which method comprises the steps of immersing the substrate as the cathode and a plate of a tin-silver alloy or tin plate as the anode in an acid tin-silver alloy plating bath which comprises a tin ion, a silver ion, one compound selected from aromatic thiol compounds and aromatic sulfide compounds, substantially no cyan compounds and a balance of water, the pH of the bath being not higher than 2, and charging electric current of about 0.5 to 50 A thereto for about 0.5 to 10 minutes to form onto the substrate a tin-silver alloy film comprising from 20 to 99 % by weight of tin and from 80 to 1 % by weight of silver and having a thickness of from 1 to 30 μm .
12. A method as claimed in claim 11, wherein the aromatic thiol compounds and aromatic sulfide compounds have from 6 to 14 carbon atoms.
13. A method as claimed in claim 11 or claim 12, wherein the aromatic thiol compounds and aromatic sulfide compounds are selected from compounds having the following structure:



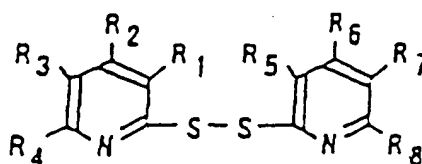
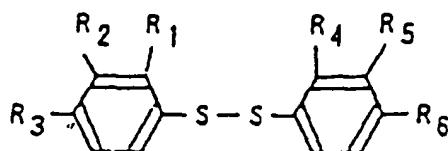
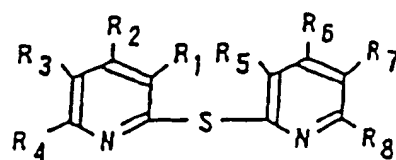
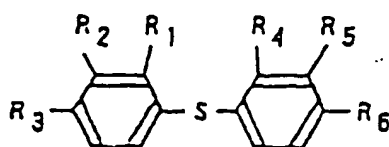
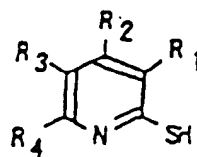
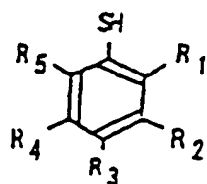


wherein R_1 to R_8 each represent a hydrogen atom, lower alkyl group, hydroxyl group, nitro group, amino group or thiol group.

14. A method as claimed in any one of claims 11 to 13, wherein the amount of the aromatic thiol compounds and aromatic sulfide compounds is from 0.1 to 200 g/l.
15. A method as claimed in any one of claims 11 to 14, wherein the amount of the tin ion is from 2 to 80 g/l calculated as Sn.
16. A method as claimed in any one of claims 11 to 15, wherein the amount of the silver ion is from 0.01 to 80 g/l calculated as Ag.
17. A method as claimed in any one of claims 11 to 16, wherein the bath further contains an acid selected from alkanesulfonic acids, alkanolsulfonic acids and sulfamic acids.
18. A method as claimed in claim 17, wherein the acid is present in an amount of from 10 to 500 g/l.

Patentansprüche

1. Saures galvanisches Bad zum Abscheiden einer Zinn-Silber-Legierung, umfassend Zinnionen, Silberionen, eine Verbindung, ausgewählt aus aromatischen Thiolverbindungen und aromatischen Sulfidverbindungen, und Wasser, wobei der pH-Wert des Bades bei 2 oder darunter liegt und wobei das Bad im Wesentlichen kein Cyanid enthält.
2. Saures galvanisches Bad nach Anspruch 1, wobei die aromatischen Sulfidverbindungen aromatische Mono- oder Disulfidverbindungen sind.
3. Saures galvanisches Bad nach Anspruch 1 oder 2, wobei die aromatischen Thiolverbindungen und die aromatischen Sulfidverbindungen 6 bis 14 Kohlenstoffatome enthalten.
4. Saures galvanisches Bad nach einem der Ansprüche 1 bis 3, wobei die Menge an aromatischen Thiolverbindungen und an aromatischen Sulfidverbindungen im Bereich von 0,1 bis 200 g/l liegt.
5. Saures galvanisches Bad nach einem der Ansprüche 1 bis 4, wobei die Menge an Zinnionen im Bereich von 2 bis 80 g/l liegt, bezogen auf Sn.
6. Saures galvanisches Bad nach einem der Ansprüche 1 bis 5, wobei die Menge an Silberionen im Bereich von 0,01 bis 80 g/l liegt, bezogen auf Ag.
7. Saures galvanisches Bad zum Abscheiden einer Zinn-Silber-Legierung nach Anspruch 1, umfassend 2 bis 80 g/l Zinnionen, bezogen auf Sn, 0,01 bis 80 g/l Silberionen, bezogen auf Ag, 0,1 bis 200 g/l einer Verbindung mit 6 bis 14 Kohlenstoffatomen, ausgewählt aus aromatischen Thiolverbindungen und aromatischen Sulfidverbindungen, und Wasser, wobei das Bad im Wesentlichen kein Cyanid enthält und wobei der pH-Wert des Bades bei 2 oder darunter liegt.
8. Saures galvanisches Bad nach einem der Ansprüche 1 bis 7, wobei die aromatischen Thiolverbindungen und die aromatischen Sulfidverbindungen aus Verbindungen mit der folgenden Struktur ausgewählt sind:



worin R_1 bis R_8 jeweils ein Wasserstoffatom, eine niedere Alkylgruppe, eine Hydroxygruppe, eine Nitrogruppe, eine Aminogruppe oder eine Thiolgruppe bedeuten.

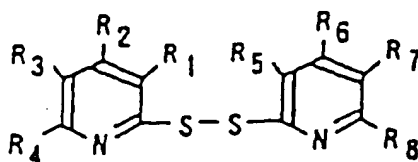
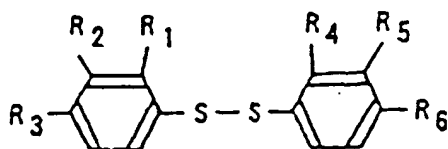
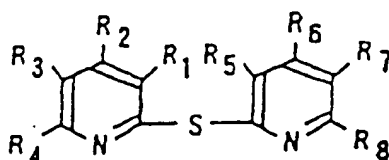
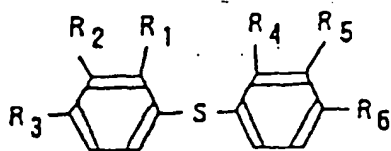
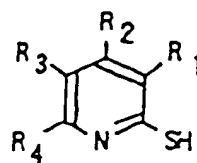
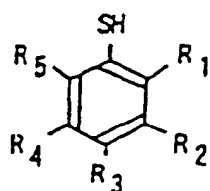
9. Saures galvanisches Bad nach einem der Ansprüche 1 bis 8, weiterhin umfassend eine Säure, ausgewählt aus der Gruppe, bestehend aus Alkansulfonsäuren, Alkanolsulfonsäuren und Sulfaminsäure.

10. Saures galvanisches Bad nach Anspruch 9, wobei die Säure in einer Menge im Bereich von 10 bis 500 g/l enthalten ist.

11. Verfahren zum galvanischen Abscheiden einer Zinn-Silber-Legierung auf einem Substrat, umfassend das Eintauchen des Substrats, das als Kathode angeordnet ist, und einer Anode, bestehend aus einer Zinn-Silber-Legierung oder aus Zinn, in ein saures galvanisches Bad zum Abscheiden einer Zinn-Silber-Legierung, umfassend Zinnionen, Silberionen, eine Verbindung, ausgewählt aus aromatischen Thiolverbindungen und aromatischen Sulfidverbindungen, und Wasser, wobei der pH-Wert des Bades bei 2 oder darunter liegt und wobei das Bad im Wesentlichen kein Cyanid enthält, wobei die Galvanisierung etwa 0,5 bis 10 Minuten lang bei einem Strom von etwa 0,5 bis 50 A durchgeführt wird, um auf dem Substrat eine Zinn-Silber-Legierung abzuscheiden, die 20 bis 99 Gew.% Zinn und 80 bis 1 Gew.% Silber enthält und die eine Dicke im Bereich von 1 bis 30 μm hat.

12. Verfahren nach Anspruch 11, wobei die aromatischen Thiolverbindungen und die aromatischen Sulfidverbindungen 6 bis 14 Kohlenstoffatome enthalten.

13. Verfahren nach Anspruch 11 oder 12, wobei die aromatischen Thiolverbindungen und die aromatischen Sulfidverbindungen aus Verbindungen mit der folgenden Struktur ausgewählt sind:



worin R_1 bis R_8 jeweils ein Wasserstoffatom, eine niedere Alkylgruppe, eine Hydroxygruppe, eine Nitrogruppe, eine Aminogruppe oder eine Thiolgruppe bedeuten.

14. Verfahren nach einem der Ansprüche 11 bis 13, wobei die Menge an aromatischen Thiolverbindungen und an aromatischen Sulfidverbindungen im Bereich von 0,1 bis 200 g/l liegt.

15. Verfahren nach einem der Ansprüche 11 bis 14, wobei die Menge an Zinnionen im Bereich von 2 bis 80 g/l liegt, bezogen auf Sn.

16. Verfahren nach einem der Ansprüche 11 bis 15, wobei die Menge an Silberionen im Bereich von 0,01 bis 80 g/l liegt, bezogen auf Ag.

17. Verfahren nach einem der Ansprüche 11 bis 16, wobei das Bad weiterhin eine Säure enthält, ausgewählt aus Alkansulfonsäuren, Alkanolsulfonsäuren und Sulfaminsäure.

18. Verfahren nach Anspruch 17, wobei der Gehalt an Säure im Bereich von 10 bis 500 g/l liegt.

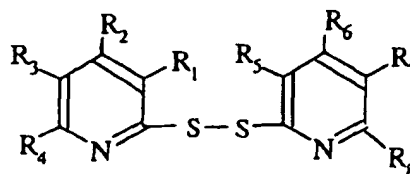
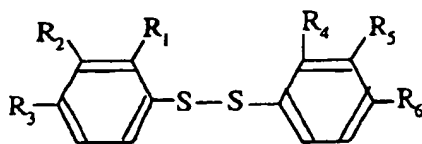
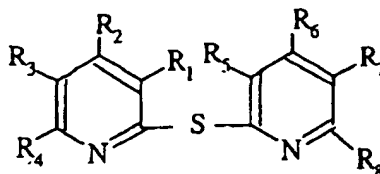
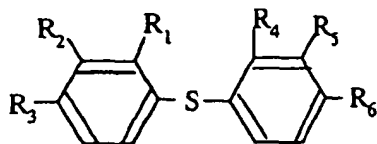
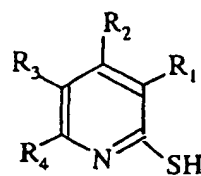
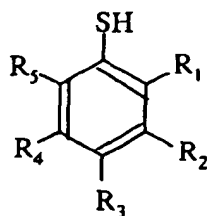
Revendications

1. Bain de placage acide d'alliage d'étain-argent qui comprend un ion étain, un ion argent, un composé choisi parmi des composés thiols aromatiques et des composés sulfures aromatiques et le reste étant de l'eau, le pH du bain n'étant pas supérieur à 2 et le bain étant pratiquement exempt de cyanure.

2. Bain de placage acide selon la revendication 1, dans lequel les composés sulfures aromatiques sont des composés mono- ou disulfures aromatiques.

3. Bain de placage acide selon la revendication 1 ou la revendication 2, dans lequel les composés thiols aromatiques et les composés sulfures aromatiques ont de 6 à 14 atomes de carbone.

4. Bain de placage acide selon l'une quelconque des revendications 1 à 3, dans lequel la quantité des composés thiols aromatiques et des composés sulfures aromatiques est comprise entre 0,1 et 200 g/l.
5. Bain de placage acide selon l'une quelconque des revendications 1 à 4, dans lequel la quantité de l'ion étain est comprise entre 2 et 80 g/l calculée en tant que Sn.
6. Bain de placage acide selon l'une quelconque des revendications 1 à 5, dans lequel la quantité de l'ion argent est comprise entre 0,01 et 80 g/l calculée en tant que Ag.
7. Bain de placage acide d'alliage d'étain-argent selon la revendication 1, lequel comprend de 2 à 80 g/l d'un ion étain calculé en tant que Sn, de 0,01 à 80 g/l d'un ion argent calculé en tant que Ag, de 0,1 à 200 g/l d'un composé ayant de 6 à 14 atomes de carbone choisi parmi des composés thiols aromatiques et des composés sulfures aromatiques, pratiquement pas de composés cyanés et le reste étant de l'eau, le pH du bain n'étant pas supérieur à 2.
8. Bain de placage acide selon l'une quelconque des revendications 1 à 7, dans lequel les composés thiols aromatiques et les composés sulfures aromatiques sont choisis parmi les composés ayant la structure suivante :



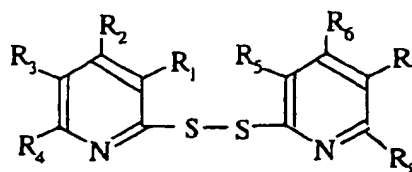
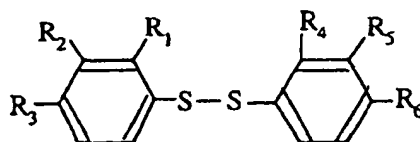
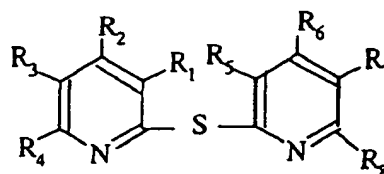
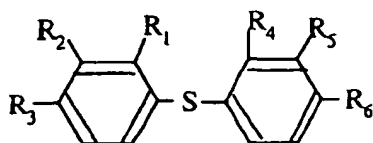
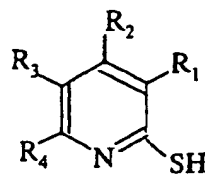
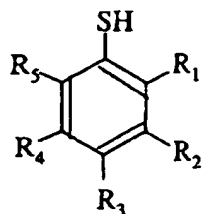
où R_1 à R_8 représentent chacun un atome d'hydrogène, un groupe alkyle inférieur, un groupe hydroxyle, un groupe nitro, un groupe amino ou un groupe thiol.

9. Bain de placage acide selon l'une quelconque des revendications 1 à 8, lequel contient en outre un acide choisi parmi des acides alcanesulfoniques, des acides alcanolsulfoniques et des acides sulfamiques.
10. Bain de placage acide selon la revendication 9, dans lequel l'acide est présent dans une quantité de 10 à 500 g/l.
11. Procédé pour le dépôt électrolytique d'un alliage d'étain-argent sur un substrat, lequel procédé comprend les étapes d'immersion du substrat en tant que cathode et d'une plaque d'un alliage d'étain-argent ou d'une plaque d'étain en tant qu'anode dans un bain de placage acide d'alliage d'étain-argent qui comprend un ion étain, un ion argent, un composé choisi parmi des composés thiols aromatiques et des composés sulfures aromatiques, pra-

tiquement pas de composés cyanés et le reste étant de l'eau, le pH du bain n'étant pas supérieur à 2, et de charge d'un courant électrique d'environ 0,5 à 50 A dans celui-ci pendant d'environ 0,5 à 10 min, pour former sur le substrat un film d'alliage d'étain-argent comprenant de 20 à 99 % en poids d'étain et de 80 à 1 % en poids d'argent et ayant une épaisseur de 1 à 30 μm .

12. Procédé selon la revendication 11, dans lequel les composés thiols aromatiques et les composés sulfures aromatiques ont de 6 à 14 atomes de carbone.

13. Procédé selon la revendication 11 ou la revendication 12, dans lequel les composés thiols aromatiques et les composés sulfures aromatiques sont choisis parmi les composés ayant la structure suivante :



où R_1 à R_8 représentent chacun un atome d'hydrogène, un groupe alkyle inférieur, un groupe hydroxyle, un groupe nitro, un groupe amino ou un groupe thiol.

14. Procédé selon l'une quelconque des revendications 11 à 13, dans lequel la quantité des composés thiols aromatiques et des composés sulfures aromatiques est comprise entre 0,1 et 200 g/l.

15. Procédé selon l'une quelconque des revendications 11 à 14, dans lequel la quantité de l'ion étain est comprise entre 2 et 80 g/l calculée en tant que Sn.

16. Procédé selon l'une quelconque des revendications 11 à 15, dans lequel la quantité de l'ion argent est comprise entre 0,01 et 80 g/l calculée en tant que Ag.

17. Procédé selon l'une quelconque des revendications 11 à 16, dans lequel le bain contient en outre un acide choisi parmi des acides alcanesulfoniques, des acides alcanolsulfoniques et des acides sulfamiques.

18. Procédé selon la revendication 17, dans lequel l'acide est présent dans une quantité de 10 à 500 g/l.